

IN THE SPECIFICATION

Please amend the Title on page 1 as follows:

AQUEOUS ELECTROLYTIC SOLUTION PRIMARY BATTERY

Please amend the paragraph at page 1, line 25 through page 2, line 12, as follows:

For example, a primary battery using aluminum as its negative electrode is expected to have high voltage, large capacity, and light weight compared with a primary battery using zinc as its negative electrode, and has been researched for a long time. For instance, the specification of United States Patent No. 2,838,591 discloses a battery comprising a positive electrode including manganese dioxide, a negative electrode made of aluminum, and an ~~electrolysis~~ electrolytic solution made of weak acidic aqueous solution of aluminum chloride. This battery, however, has a problem in reactivity between the aluminum used in the negative electrode and the ~~electrolysis~~ electrolytic solution, and is hence large in self-discharge, large in generation of hydrogen gas, and small in capacity.

Please amend the paragraph at page 3, lines 1-12, as follows:

On the other hand, according to Jpn. Pat. Appln. KOKAI Publication No. 8-77996, a water repellent polymer sheet having gas permeable and liquid impermeable properties is provided between the gasket and the negative electrode bottom plate, and the gas in the battery is forced outside the battery, and leakage or scattering of ~~electrolysis~~ electrolytic solution to the outside of the battery is prevented.

Please amend the paragraph at page 6, line 11 through page 7, line 3, as follows:

A first battery of the invention comprises:

a power generating element container,

a tubular positive electrode mixture provided inside of the power generating element container,

a bag-like separator provided in a hollow space of the positive electrode mixture,

a negative electrode gel accommodated in the separator and containing a negative electrode active material and an aqueous ~~electrolysis~~ electrolytic solution, and

a hydrogen gas permeable sheet provided in the opening of the power generating element container, the hydrogen gas permeable sheet having a water repellence of 2 kPa or more and a He gas permeability at 30°C in a range of  $2 \times 10^{-6}$  to  $10000 \times 10^{-6}$  (cm<sup>3</sup> (STP) cm/sec·cm<sup>2</sup>·cmHg),

in which the inner surface of the hydrogen gas permeable sheet is inclined so that the distance between the inner surface and the positive electrode mixture gradually decreases toward a side wall of the power generating element container.

Please amend the paragraph at page 8, line 26 through page 9, line 15, as follows:

A positive electrode can (power generating element container) 9 of cylindrical form with bottom functioning as a positive electrode current collector is inserted into the package 1 with the opening facing downward. This positive electrode can 9 may be formed of, for example, a positive electrode current collector component material described below. A cylindrical positive electrode mixture 10 is contact with the inner surface of the side wall of the positive electrode can 9. A separator 11 of cylindrical form with bottom is provided in a hollow space of the positive electrode mixture 10. A negative electrode gel 12 fills up the separator 11. An ~~electrolysis~~ electrolytic solution is held in the negative electrode gel 12, separator 11 and positive electrode mixture 10. The negative electrode current collector 6 is inserted into the negative electrode gel 12.

Please amend the paragraph at page 10, line 24 through page 11, line 19, as follows:

In the aluminum negative electrode battery of such structure, when discharge reaction progresses, discharge product of the negative electrode (for example, aluminum hydroxide) starts remaining between the separator 11 and negative electrode gel 12. Herein, if the dissolution of the discharge product of the negative electrode is low and the diffusion speed of the discharge product is low due to some reason, water molecules are collected at the negative electrode side of the separator by osmotic phenomenon. Since the volume of the gap between the separator 11 and negative electrode gel 12 is small, the collected ~~electrolysis~~ electrolytic solution cannot be held therein. If a gas permeable water repellent polymer film is arranged between the gasket and bottom plate, for example, as disclosed in Jpn. Pat. Appln. KOKAI Publication No. 8-77996, electrolyte leakage cannot be prevented sufficiently, the ~~electrolysis~~ electrolytic solution collected between the water repellent polymer film and gasket cannot return to the power generating element, and the ~~electrolysis~~ electrolytic solution in the power generating element is insufficient, and high discharge capacity cannot be achieved, as clarified by the present inventor.

Please amend the paragraph at page 11, line 27 through page 13, line 2, as follows:

The inventor repeated intensive studies, and discovered that the ~~electrolysis~~ electrolytic solution overflowing from the negative electrode and separator can be returned to the positive electrode as indicated by an arrow in FIG. 1 without leaking outside of the battery, by arranging the hydrogen gas permeable sheet 13 between the inner surface of the opening of the positive electrode can (power generating element container) 9 and the negative electrode gasket 4 so as to enclose the power generating elements that includes the positive electrode mixture 10, separator 11 and negative electrode gel 12 in the positive electrode can 9, and inclining the peripheral edge of the hydrogen gas permeable sheet 13 so that the

distance between the sheet 13 and the positive electrode mixture 10 may decrease from the center of the positive electrode can 9 toward the side wall, or along the radial direction. Hydrogen gas generated by discharge reaction passes through the hydrogen gas permeable sheet 13, and sequentially passes through the gas vent hole 5 of the negative electrode gasket 4 and the gas vent hole 8 of the metal washer 7, and further passes through very narrow gap existing between the bottom plate 2 and package 1 and the gas vent hole 3a of the bottom plate 2, and is released to outside, and therefore evaporation of ~~electrolysis~~ electrolytic solution is suppressed to a minimum limit, and hydrogen gas can be forced out of the battery. Hence, the invention can enhance the discharge capacity and suppress electrolyte leakage at the same time.

Please amend the paragraph at page 13, lines 3-22, as follows:

The inclination angle  $\theta_1$  is preferred to be in a range of 3 degrees to 65 degrees. The reason is as follows. If the inclination angle  $\theta_1$  is smaller than 3 degrees, the ~~electrolysis~~ electrolytic solution overflowing from the power generating elements hardly returns to the positive electrode, and the discharge capacity may drop or the leak rate may increased. On the other hand, if the inclination angle  $\theta_1$  is more than 65 degrees, the active material filling amount is insufficient, and large capacity may not be achieved. A more preferred range of inclination angle  $\theta_1$  is 15 degrees to 45 degrees. When the inclination angle  $\theta_1$  is in a range of 15 degrees to 45 degrees, a battery of high discharge capacity and low leak rate is achieved. In FIG. 1 and FIG. 2, only the peripheral edge of the hydrogen gas permeable sheet 13 is inclined, but the entire surface may be inclined. As shown in FIG. 1 and FIG. 2, both surfaces of the hydrogen gas permeable sheet 13 may be inclined, but only the surface opposite to the power generating element may be inclined.

Please amend the paragraph at page 13, line 23 through page 14, line 10, as follows:

In FIG. 1 and FIG. 2, the hydrogen gas permeable sheet 13 contacts with part of the power generating elements (in this case, the end face of the separator 11), but the hydrogen gas permeable sheet 13 may be installed apart from the power generating elements, and an air space may be formed between the power generating elements and the hydrogen gas permeable sheet. As a result, the ~~electrolysis~~ electrolytic solution can be circulated more smoothly from the interface of the negative electrode gel 12 and the separator 11 toward the positive electrode direction, and the occurrence rate of electrolyte leakage can be further lowered. At the same time, the generated hydrogen gas may be temporarily held in the air space, and sudden elevation of internal pressure can be avoided.

Please amend the paragraph at page 15, lines 24-27, as follows:

The positive electrode, negative electrode, separator, ~~electrolysis~~ electrolytic solution, and hydrogen gas permeable sheet used in the first battery of the invention are specifically described below.

Please amend the paragraph at page 19, lines 4-5, as follows:

The positive electrode may be used by mixing with the ~~electrolysis~~ electrolytic solution described later.

Please amend the paragraph at page 19, lines 16-25, as follows:

The purity of the negative electrode metal is 99 wt.% or more, that is, the impurity should be 1 wt.% or less. In particular, in the case of aluminum, the purity should be 99.5 wt.% or more, that is, aluminum with impurity of 0.5 wt.% or less should be used. If the

impurity is contained by more than 0.5 wt.%, it is likely to be corroded by the ~~electrolysis~~ electrolytic solution, and violent self-discharge or gas generation may take place. A more preferred range of purity is 99.9 wt.% or more.

Please amend the paragraph at page 20, lines 8-13, as follows:

The negative electrode may be used by mixing preliminarily with the ~~electrolysis~~ electrolytic solution described below. That is, a negative electrode gel containing negative electrode active material, ~~electrolysis~~ electrolytic solution, and polymer for holding this ~~electrolysis~~ electrolytic solution may be used.

Please amend the paragraph at page 20, lines 14-16, as follows:

The surface of the negative electrode may be coated with an additive explained in the following section 4) of ~~electrolysis~~ electrolytic solution.

Please amend the paragraph at page 20, lines 18-22, as follows:

The separator is composed of, for example, insulating material. The ~~electrolysis~~ electrolytic solution is held in the separator, and the ionized electrolyte must be movable in the ~~electrolysis~~ electrolytic solution, and hence the separator is preferably made of porous material.

Please amend the paragraph at page 21, lines 8-17, as follows:

If the positive electrode and negative electrode are provided so as not to contact with each other, and the battery structure is designed to hold the ~~electrolysis~~ electrolytic solution between the positive electrode and negative electrode, the separator is not always required. Alternately, by adding a thickener to the ~~electrolysis~~ electrolytic solution to be subjected to

gel, a solid electrolyte may be used. In this case, the thickener phase functions as the separator, and the ~~electrolysis~~ electrolytic solution phase is held in the thickener phase.

Please amend the paragraph at page 21, line 20 through page 22, line 1, as follows:

The ~~electrolysis~~ electrolytic solution contains an electrolyte and a solvent for dissolving the electrolyte. It is preferred to add an additive to the ~~electrolysis~~ electrolytic solution for suppressing corrosive reaction between the ~~electrolysis~~ electrolytic solution and negative electrode. The ~~electrolysis~~ electrolytic solution may also contain other additives for other purposes than suppression of corrosive reaction between the ~~electrolysis~~ electrolytic solution and negative electrode.

Please amend the paragraph at page 22, lines 3-8, as follows:

The electrolyte is a compound supplying at least one ion (called first ion hereinafter) of sulfate ion ( $\text{SO}_4^{2-}$ ) and nitrate ion ( $\text{NO}_3^-$ ) in a solvent. By supplying such highly reactive ion such as sulfate ion ( $\text{SO}_4^{2-}$ ) and nitrate ion ( $\text{NO}_3^-$ ) in the ~~electrolysis~~ electrolytic solution, the obtained battery has a high output.

Please amend the paragraph at page 22, lines 12-27, as follows:

The amount of electrolyte in the ~~electrolysis~~ electrolytic solution is preferred to be the concentration of the first ion in a range of 0.2 to 16 M/L. If the concentration of the first ion is less than 0.2 M/L, the ion conductivity may be lowered. When containing an additive to the ~~electrolysis~~ electrolytic solution, it may be hard to form the film containing the additive sufficiently on the negative electrode surface, and corrosive reaction of the negative electrode may not be suppressed sufficiently. On the other hand, if the concentration of the first ion

exceeds 16 M/L, the film growth on the negative electrode surface is significant, and the interface resistance of the negative electrode is increased, and high voltage may not be achieved. A more preferred range is 0.5 to 10 M/L.

Please amend the paragraph at page 23, line 26 through page 24, line 7, as follows:

On the other hand, aside from the battery reaction, for example, when sulfuric acid aqueous solution is used as the ~~electrolysis~~ electrolytic solution, the aluminum of the negative electrode is likely to be corroded by the sulfuric acid (self-discharge) as shown in formula (3). The first ion is high in reactivity, and is high in battery output, and is also high in the reactivity of the corrosive reaction shown in formula (3).

Please amend the paragraph at page 24, lines 9-15, as follows:

The additive component existing on the negative electrode surface is low in electron conductivity, and hence can impede electron exchange between the sulfuric acid contained in the ~~electrolysis~~ electrolytic solution and the aluminum of the negative electrode, so that the corrosive reaction of the negative electrode can be suppressed.

Please amend the paragraph at page 28, line 14 through page 29, line 4, as follows:

The He gas permeability coefficient at 30°C of hydrogen gas permeable sheet is specified in the range mentioned above because if the He gas permeability coefficient is less than  $2 \times 10^{-6}$  (cm<sup>3</sup> (STP) cm/sec·cm<sup>2</sup>·cmHg), the hydrogen gas permeability is lowered, and hydrogen gas is remained in the enclosed space containing the power generating elements, and the equilibrium of the discharge reaction is broken to lower the discharge capacity of the battery. If the He gas permeability coefficient exceeds  $10000 \times 10^{-6}$  (cm<sup>3</sup> (STP)



cm/sec·cm<sup>2</sup>·cmHg), the hydrogen gas permeability is higher, but other gas than hydrogen gas (such as steam) may also permeate. If steam permeates, the ~~electrolysis~~ electrolytic solution may lose its water and the capacity may be lowered. A more preferred range is  $2 \times 10^{-6}$  to  $1000 \times 10^{-6}$  (cm<sup>3</sup> (STP) cm/sec·cm<sup>2</sup>·cmHg), and most preferred range is  $2 \times 10^{-6}$  to  $400 \times 10^{-6}$  (cm<sup>3</sup> (STP) cm/sec·cm<sup>2</sup>·cmHg).

Please amend the paragraph at page 29, lines 5-18, as follows:

The water repellency of the hydrogen gas permeable sheet is limited in the specified range because if the water repellency is less than 2 kPa, leakage of ~~electrolysis~~ electrolytic solution due to creeping phenomenon cannot be suppressed, and the ~~electrolysis~~ electrolytic solution may ooze out of the hydrogen gas permeable sheet, and the ~~electrolysis~~ electrolytic solution cannot be returned to the positive electrode. A more preferred range is 5.3 kPa or more. A most preferred range is 9.3 kPa or more. At higher water repellency, the effect of prevention of electrolyte leakage is higher, but if the water repellency is too high, the He gas permeability coefficient at 30°C becomes smaller than  $2 \times 10^{-6}$  (cm<sup>3</sup> (STP) cm/sec·cm<sup>2</sup>·cmHg), which is not preferable.

Please amend the paragraph at page 31, line 13 through page 32, line 5, as follows:

The second battery of the invention comprises:

a negative electrode container,

a positive electrode mixture provided in the negative electrode container, and

impregnated with an aqueous ~~electrolysis~~ electrolytic solution,

a separator provided between the inner surface of the negative electrode container and the positive electrode mixture, and

a hydrogen gas permeable sheet provided in the opening of the negative electrode container, the hydrogen gas permeable sheet having a water repellence of 2 kPa or more and a He gas permeability at 30°C in a range of  $2 \times 10^{-6}$  to  $10000 \times 10^{-6}$  (cm<sup>3</sup> (STP) cm/sec·cm<sup>2</sup>·cmHg),

in which the inner surface of the hydrogen gas permeable sheet is inclined so that the distance between the inner surface and the positive electrode mixture may decrease from the side wall of the negative electrode container toward the central part in the radial direction.

Please amend the paragraph at page 32, lines 19-25, as follows:

As shown in FIG. 3, a negative electrode can 31 of cylindrical form with bottom made of aluminum or aluminum alloy is filled with a positive electrode mixture 34 containing a positive electrode active material, a conductive agent, and an aqueous ~~electrolysis~~ electrolytic solution, by way of a separator 32 and a bottom paper 33.

Please amend the paragraph at page 34, line 26 through page 35, line 22, as follows:

That is, by arranging the hydrogen gas permeable sheet 39 in the air space 38, the power generating elements that includes the positive electrode mixture 34 and separator 32 are enclosed in the negative electrode can 31, and further by inclining the hydrogen gas permeable sheet 39 so that the distance between the sheet 39 and power generating elements may decrease from the side wall of the negative electrode can 31 toward the center, or along the radial direction, it is discovered that the electrolyte overflowing from the negative electrode and separator can be returned to the positive electrode as indicated by an arrow in FIG. 3 without any leak to outside of the battery. Besides, the hydrogen gas generated by discharge reaction passes through the hydrogen gas permeable sheet 39, and sequentially passes through the gas vent hole 35 of the insulating washer 36 and gas vent hole 45 of the

sealing plate 44, and is released outside, and therefore the hydrogen gas can be released outside of the battery while the evaporation of ~~electrolysis~~ electrolytic solution is minimized. Therefore, according to the invention, both enhancement of discharge capacity and suppression of electrolyte leakage can be achieved.

Please amend the paragraph at page 35, lines 23-26, as follows:

The positive electrode, negative electrode, separator, ~~electrolysis~~ electrolytic solution, and hydrogen gas permeable sheet used in the second battery may be the same as those explained in the first battery.

Please amend the paragraph at page 36, lines 10-21, as follows:

In FIG. 3, the hydrogen gas permeable sheet 39 is arranged apart from the power generating element, and when a space is thus formed between the power generating element and hydrogen gas permeable sheet 39, the ~~electrolysis~~ electrolytic solution can be returned smoothly from the interface of the negative electrode can 31 and separator 32 to the positive electrode, and the electrolyte leakage occurrence may be much lowered. This space also function as a space for temporarily holding the generated hydrogen gas, and elevation of internal pressure due to generation of hydrogen gas can be lessened.

Please amend the paragraph at page 37, line 16 through page 38, line 8, as follows:

An annular water repellent layer of contact angle with water of 70 degrees or more should be preferably formed on the inner surface of the side wall of the negative electrode case and positioned between the power generating element and hydrogen gas permeable sheet 39. As a result, the electrolyte leakage rate is further lowered. That is, along with the progress of discharge, discharge product such as aluminum hydroxide is contained in the

~~electrolysis~~ electrolytic solution at high concentration, and the surface tension of the ~~electrolysis~~ electrolytic solution is raised, and the ~~electrolysis~~ electrolytic solution is likely to leak out through the wall of the negative electrode can 31. The water repellent layer suppresses creeping of the ~~electrolysis~~ electrolytic solution over the separator 32, and electrolyte leakage outside of the battery can be reduced. Moreover, by forming the water repellent layer at a position closer to the upper end of the positive electrode mixture 34, it is effective to return the creeping ~~electrolysis~~ electrolytic solution back to the positive electrode.

Please amend the paragraph at page 39, lines 9-24, as follows:

A third battery of the invention comprises:

a battery case,

a power generating element stored in the battery case and including an aqueous ~~electrolysis~~ electrolytic solution, and

a hydrogen gas permeable sheet provided in the opening of the battery case, the hydrogen gas permeable sheet having a water repellence of 2 kPa or more and a He gas permeability at 30°C in a range of  $2 \times 10^{-6}$  to  $10000 \times 10^{-6}$  (cm<sup>3</sup> (STP) cm/sec·cm<sup>2</sup>·cmHg),

in which the hydrogen gas permeable sheet has a surface that faces the power generating element and has recesses satisfying the following formula (1).

$$0.01X \leq D \leq 0.95X \quad (1)$$

where D is a depth (μm) of each recess, and X is the thickness (μm) of the hydrogen gas permeable sheet.

Please amend the paragraph at page 41, line 10 through page 42, line 15, as follows:

Flange paper is not necessary when the hydrogen gas permeable sheet 39 is installed, but it may be provided. In such a case, if it is arranged between the positive electrode

mixture 34 and hydrogen gas permeable sheet 39, the circulation of the ~~electrolysis~~ electrolytic solution is disturbed. It is preferred to arrange the flange paper between the insulating washer 36 and the hydrogen gas permeable sheet 39. If the flange paper or washer is plurally provided, although the electrolyte leakage preventive effect is improved, the filling amount of the battery active material is decreased, and it is preferred to use one piece only. The washer and positive electrode terminal plate are desired to have gas vent holes for releasing the gas generated in the battery. The hole should be provided with a rubber valve or the like so as to be opened and closed repeatedly. Alternately, by arranging the hydrogen gas permeable sheet by overlaying at the inner surface do as to cover the hole of the washer or positive electrode terminal plate, the function as gas vent hole is realized. Alternately, instead of opening a hole, in particular, gas may be released outside of the battery through a gap between the washer and negative electrode can 31 or a gap between the washer 36 and positive electrode current collector 37 depending on the size of the gap. Alternately, as a safety valve in the case of abnormal discharge, a thinnest wall may be formed by cutting off part of the hydrogen gas permeable sheet 39, flange paper, washer, positive electrode terminal plate 44 or negative electrode can 31. The thickness  $t$  of the thinnest wall is preferred to be in a range of 5 to 300  $\mu\text{m}$ .

Please amend the paragraph at page 43, line 3, as follows:

<Preparation of ~~electrolysis~~ electrolytic solution>

Please amend the paragraph at page 43, lines 8-13, as follows:

By mixing 95 wt.% of aluminum powder with purity of 99.99% (4N) and 4 wt.% of acrylic acid polymer as thickener, ~~electrolysis~~ electrolytic solution was added thereto and a

negative electrode gel was prepared. As negative electrode current collector, a stainless steel bar was prepared.

Please amend the paragraph at page 44, line 2 through page 45, line 5, as follows:

In the positive electrode can 9 of cylindrical form with bottom serving also as positive electrode current collector, a cylindrical positive electrode mixture 10 and a bag-shaped separator 11 formed of a glass fiber sheet having a thickness of 30  $\mu\text{m}$  were provided, and the separator 11 was filled with negative electrode gel 12, and ~~electrolysis~~ electrolytic solution was poured into the positive electrode mixture 10, separator 11 and negative electrode gel 12. Then, a negative electrode current collector 6 was inserted into the negative electrode gel 12. In succession, a water repellent organic polymer sheet 13 was interposed between the inner circumference of the positive electrode can 9 and the thick wall 4a of the negative electrode gasket 4 so that the distance between the upper surface of the sheet 13 and the lower surface of the positive electrode mixture 10 may decrease from the center of the positive electrode can to the side wall. The outer circumference of the water repellent organic polymer sheet 13 was joined to the inner circumference of the positive electrode can 9 by means of silicone rubber liquid gasket 14b (junction limit pressure measured by pressure resisting test of JIS K 6820 of 10  $\text{kgf/cm}^2$ ), and the inner circumference of the sheet 13 was joined to the periphery of the thick wall 4a of the negative electrode gasket 4 by means of silicone rubber liquid gasket 14a (junction limit pressure measured by pressure resisting test of JIS K 6820 of 10  $\text{kgf/cm}^2$ ). The water repellent organic polymer sheet 13 was brought into contact with the lower side of the separator 11.

Please amend the paragraph at page 50, line 26 through page 51, line 5, as follows:

An electrolytic manganese dioxide as positive electrode active material, acetylene black as conductive agent, and an ~~electrolysis~~ electrolytic solution formed of a mixed aqueous solution containing 1 M of  $\text{AlCl}_3$ , 0.1 M of 2,2-bipyridyl, 0.5 M of KCl, and 0.2 M of  $\text{Al}(\text{NO}_3)_3$  was mixed at a ratio of 20: 2: 15 by weight, and a positive electrode mixture was prepared.